

## Light curing type paint resin for shade adjustment

The invention relates to a photocurable dental coating material, suitable for color correction of dental restorations or artificial teeth.

### Background of the invention

In order to satisfy the esthetic elements in dental prosthetic treatment, methods of using not only metals but also ceramics and resins for facings can recreate corona color. Among them, the development of resins is remarkable, and some with the capability of having physical strength with sufficient abrasion resistance (chewing resistance, withstanding tooth brushing) have started to appear. To further improve the esthetics of such rigid resin for dental use, dental technicians are hard at work on the production of prosthetic materials by employing various methods.

One such method is staining, in which colored gel state stain material is used to perform the desired shade adjustment and to characterize the facing. In this method, gel state paste will be colored with a brush, so the operability of the stain material must be high. For that reason, the viscosity and degree of polymerization has been regarded as more important than abrasion resistance, and thus either filler would not be filled in, or even if it were, it was limited only to a small amount of fine filler. Therefore, the brush abrasion resistance on the prosthetic surface was at such a low level that it could not be used clinically, and thus the staining was used only in the rigid resin sandwich method (internal stain method).

However, the sandwich method had negative factors such as those below:

1. The stain shade nuance changed depending on the hue and thickness of the rigid resin covering the stain, and therefore,
2. the sandwich method only allowed skilled technicians to use it precisely, and
3. it could not be used for the final adjustment.

In many countries the law prohibits dental technicians who are the principal technicians in dental technique to see the patient directly and participate in treatment. Therefore, the prosthetic is produced strictly under the instructions of a dentist. At such time, in many cases the hue specifications, are conducted according to a hue guide, e.g. the VITA<sup>®</sup> Shade Guide which is classi-

fied into 16 colors. However, this cannot reflect the natural tooth color of a patient accurately, and thus a small offset in color and aberration has resulted in many cases. Also, natural teeth have opaque bands and dots, topological hue variations as well as discoloration from external factors (such as smoking), and thus differences between individuals are great.

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Since rigid resin in dentistry requires a high surface smoothness, it is the general practice to use a small as possible diameter particle filler." In the early days of the conventional product, although there were some dentists using poly (methyl methacrylate) (PMMA) spherical particle, they had a big problem with durability (abrasion resistance) due to severe wear in the PMMA area. Ultra fine silica of approximately 40 nm in mean particle diameter that is produced through spray thermal decomposition of tetrachlorosilane is generally used for conventional products in recent years. For example, US 5,009,597 proposes a shell or jacket material for crowns which contains 30-70% by weight of microdispersed silicon dioxide, preferably of a particle size from 0.01-0.04 micrometers. EP 475 239 B1 concerns a filler mixture of (A) nano-sized spherical  $\text{SiO}_2$  with 20% high refractive index oxides and (B) micro-sized quartz, ceramic or glass powder, as well as optionally pyrogenic silica as rheological modifier. DE 196 157 63 A1 describes a filler of porous  $\text{SiO}_2$  glass of 20-120 nm which is purported to give good abrasion resistance in dental composite materials. DE 44 46 033 C2 relates to fine particle silica fillers with a sheet crystal structure.

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However, when such ultra fine particles are used, the completed resin paste increases the viscosity rapidly when the amount of ultra fine particle increases, and thus the resin paste becomes very difficult to handle in terms of dental technique operation. Therefore, the conventional product generally has a problem of not being able to increase the filler content higher than a certain amount.

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In rigid resin for dental technique (for crown restoration), to some degree a solution has been found thanks to the development of organic composite filler. The organic composite filler was created by crushing the paste with a high content ratio of thoroughly kneaded ultra fine particle filler after it was cured. Since it was a filler with a mean particle diameter of several  $\mu\text{m}$  or more, the paste containing the filler shows characteristics and conditions as if it were a crushed type of filler containing resin. It behaves like an ultra fine filler containing resin when grinding it that makes it easy to obtain a very smooth surface. Nonetheless, from the viewpoint of the inorganic filler content's amount, it remains at approximately 50% by mass, and the mechanical characteristic was not all that high.

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However, for the light curing type of paint resin for shade adjustment, it is desirable to have a paint resin for the purpose of hue adjustment of the rigid resin veneered crown. In other words, it is necessary to make a paste having sufficient viscosity to make an application work with use of a brush possible while improving the mechanical strength. In particular, wear and abrasion resistance capability is indispensable.

Conventional rigid resins have to be built up by use of such means as a spatula for shaping, the paste must be in clay form with a certain shape retaining capability. However, since the stain material for such purpose, as the light curing type of paint resin for shade adjustment in this patent application, requires a paint resin application and fine manipulation with use of a brush, it must be in a gel form paste.

DE 38 39 069 A1 describes a method for coating dental restorative parts produced by CAD/CAM methods. A thin pigmented coating is applied, followed by a second glossy anti-abrasive transparent sealant. The sealant has a preferred inorganic filler content of more than 40% and is preferably ultra fine particle silica. The pigmented coating should be of low viscosity to give a very thin layer. Abrasion resistance is not a requirement for the pigmented coating.

The object of the present invention is to develop stain material for the final shade adjustment as a tool which can be used for a prosthetic surface (e.g. all kinds of crowns, bridges, veneers, inlays) and artificial teeth (e.g. removable or fixed, partial- and full dentures), enabling the user to produce a prosthetic with a hue of more natural appearance close to the natural dental color of a patient. Desired is a photocurable coating material for color correction of dental restorations or teeth, which is flowable, of paste-like or paint-like viscosity, applicable by a brush or similar instrument, capable to give a smooth and glossy surface after curing, and which produces an abrasion resistant coating on the surface of a tooth or a dental restoration in a desired color shade.

#### Summary of the invention

In one embodiment the object of the present invention is achieved by a material comprising a matrix resin and an inorganic filler - while maintaining sufficient fluidity for making an application of the paint resin with a brush possible. The material comprises (A) 40 - 60% by mass of matrix resin, (B) 60 - 40% by mass of a filler mixture; (C) 0.1 - 1% by mass of one or more polymerization initiator(s); and (D) trace quantities of one or more dental pigments.

## Detailed description

When implementing the invention, an existing widely known matrix resin can be used (Shin Zairyo Shin Sozai Series Saishin Shika Zairyo Oyobi Gijutsu Kiki (New Materials Series: Latest Dental Materials), edited by Hasegawa Jiro (Jiro Hasegawa) and published by Kabushikigaisha CMC, Pages 7-18). Normally, methacrylate monomer, especially polymerizable multifunctional methacrylate, which can form a bridge structure after curing, is used as the matrix monomer by considering safety for the organism.

Suitable free radically-polymerizable monomers may contain at least one ethylenically-unsaturated bond, can be oligomers or polymers, and are capable of undergoing addition polymerization. Such monomers include mono-, di- or poly- acrylates and methacrylates such as methyl acrylate, methyl methacrylate, ethyl acrylate, isopropyl methacrylate, n-hexyl acrylate, stearyl acrylate, allyl acrylate, glycerol diacrylate, glycerol triacrylate, ethyleneglycol diacrylate, diethyleneglycol diacrylate, triethyleneglycol dimethacrylate, 1,3-propanediol diacrylate, 1,3-propanediol dimethacrylate, trimethylolpropane triacrylate, 1,2,4-butanetriol trimethacrylate, 1,4-cyclohexanediol diacrylate, pentaerythritol triacrylate, pentaerythritol tetraacrylate, pentaerythritol tetramethacrylate, sorbitol hexacrylate, bis[1-(2-acryloxy)]-p-ethoxyphenyldimethylmethane, bis[1-(3-acryloxy-2-hydroxy)]-p-propoxyphenyldimethylmethane, tris(hydroxyethylisocyanurate)-trimethacrylate; the bis-acrylates and bis-methacrylates of polyethylene glycols of molecular weight 200-500, copolymerizable mixtures of acrylated monomers such as those of U.S. Pat. No. 4,652,274, incorporated herein by reference, and acrylated oligomers such as those of U.S. Pat. No. 4,642,126, incorporated herein by reference; unsaturated amides such as methylene bis-acrylamide, methylene bis-methacrylamide, 1,6-hexamethylene bisacrylamide, diethylene triamine tris-acrylamide and beta-methacrylamino-ethyl methacrylate; and vinyl compounds such as styrene, diallyl phthalate, divinyl succinate, divinyl adipate and divinylphthalate. Mixtures of two or more monomers can be used if desired. Preferably, the free radically polymerizable material used is mono-, di-, or poly-acrylates and methacrylates such as methyl acrylate, methyl methacrylate, ethyl acrylate, glycidyl methacrylate, 2-isocyanatoethyl methacrylate, limonene oxide, isopropyl methacrylate, n-hexyl acrylate, stearyl acrylate, allyl acrylate, glycerol diacrylate, glycerol triacrylate, ethyleneglycol diacrylate, diethyleneglycol diacrylate, triethyleneglycol dimethacrylate, 1,3-propanediol diacrylate, 1,3-propanediol dimethacrylate, trimethylolpropane triacrylate, 1,2,4-butanetriol trimethacrylate, 1,4-cyclohexanediol diacrylate, pen-

terthritol triacrylate, pentaerythritol tetracrylate, pentaerythritol tetramethacrylate, sorbitol hexacrylate, bis[1-(929acryloxy)]-p-ethoxyphenyl dimethylmethane, bis[1-(3-acryloxy-2-hydroxy)]-p-propoxyphenyldimethylmethane, and trihydroxyethyliso-cyanurate trimethacrylate; the bisacrylates and bis-methacrylates of polyethylene glycols of molecular weight 200-500, copolymerizable mixtures of acrylated monomers such as those in U.S. Pat. No. 4,652,274, and acrylated oligomers such as those of U.S. Pat. No. 4,642,126; and vinyl compounds such as styrene, diallyl phthalate, divinyl succinate, divinyl adipate and divinylphthalate. Mixtures of two or more of these free radically polymerizable materials can be used if desired.

- Two types of matrix monomers are mainly used, and they are: bisphenol A, having a relatively large molecular weight and small shrinkage after cure, as the fundamental structure and another one having a urethane structure. It is common practice to combine them with monomers such as a dimethacrylate monomer having an ethylene glycol chain for the purpose of adjusting viscosity and, refraction index for use.
- Preferred monomers are bisphenol-A-glycidyl dimethacrylate (bis-GMA), Bisphenol-A-Ethoxydimethacrylate, 2,2-bis[4-(2-hydroxy-3-methacryloxypropoxy)phenyl]propane, polymeric ethoxylated Bisphenol A dimethacrylates (Bis-EMA), Bis EMA (2,6), Bis EMA(6), triethylene glycol dimethacrylate (TEGDMA), 1,6-bis(methacryloxy-2-ethoxycarbonylamino)-2,4,4-trimethylhexan (UDMA).
- A widely known existing initiator (light polymerization catalysis) can be used (New Materials Series: Latest Dental Materials), edited by Hasegawa Jiro (Jiro Hasegawa) and published by Kabushikigaisha CMC, Page 19). Radical polymerization is normally employed for a composite resin curing reaction. The initiators are classified into the chemical polymerization type products that use a redox initiator composed of a combination of benzoyl peroxide/aromatic amine (R3N), and the light curing type of products that use a visible light polymerization initiator composed of a combination of camphorquinone/aromatic amine (R3N). However, single pastes of them are possible, and thus the mainstream is the light curing type products with no grinding required and no air bubble contamination. Examples of suitable photoinitiators are benzophenone, benzoin and their derivatives or alpha-diketones and their derivatives, such as 9,10-phenanthrenequinone, diacetyl or 4,4-dichlorobenzil; and alpha-diketones in combination with amines as reducing agents, such as e.g. cyanoethylmethylaniline, methylaminoethylmethacrylate, triethanolamine, N,N-dimethyl-sym.-xylidine. Further suitable photoinitiators are acyl phosphines, such as e.g. 2,4,6-trimethylbenzoyl-diphenyl- or bis(2,6-dichlorobenzoyl)-4-N-propylphenylphosphin oxide.

Camphorquinone is especially suitable.

A widely known existing filler mixture, which is made of silicon dioxide and surface treated silicon dioxide, can be used (New Materials Series: Latest Dental Materials), edited by Hasegawa Jiro (Jiro Hasegawa) and published by Kabushikigaisha CMC, Pages 16-17). A typical composite resin can be classified by the type of a large amount of the filler used for filling it. For example, it can be classified by particle diameter such as follows:

- (1) Larger than 1  $\mu\text{m}$  (macro particle filling type)
- (2) 0.1  $\mu\text{m}$  - 1  $\mu\text{m}$  (sub micron particle filling type)
- (3) Smaller than 0.1  $\mu\text{m}$  (ultra fine particle filling type)
- (4) A mixture of different diameter particle fillers of the above.

In some cases, it is classified by a diameter of 3  $\mu\text{m}$ . As for particle geometry, there are shapeless, spherical shape and fabric shape.

When viewed from the composition aspect, barium aluminosilicate glass, silica, zirconia, metal and non metal oxides and their mixtures and cracked polymer (splinter polymer) containing ultra fine particles can be listed. Although various treatment agents as well as methods are employed for such surface treatment, normally a polymerizable functional group is introduced to the silanol on the filler surface by a silane compound such as a gamma-methacryl oxypropyl trimethoxy silane (Silane A 174) in order to gain affinity to the matrix.

The filler mixture of the present invention is preferably made up of silicon dioxide 40 - 60 % by mass and silicone dioxide splinter polymer 60 - 40 % by mass. The silicon dioxide splinter polymer is preferably silicon dioxide/polydodecanediol dimethacrylate. Of course similar splinter polymers will also be suitable for the compositions of the invention. Suitable splinter polymers are produced by polymerizing (meth)acrylate monomers in the presence of silicon dioxide powders and subsequent grinding of the resulting material.

A preferred composition comprises about 50% by mass matrix resin, about 49% by mass filler mixture, and about 1% by mass initiator.

Especially preferred are compositions comprising: 19 % by mass bisphenol A diglycidyl acrylate, 11% by mass urethane methacrylate, triethylene glycol dimethacrylate, silicon dioxide 23%

by mass, 22% by mass silicon dioxide/polydodecanediol dimethacrylate 24,4 % by mass, and 0.6% by mass initiator.

5 The intended use for shade adjustment purposes usually requires the presence of pigments, that are common in the dental field.

Especially preferred pigments are iron-oxides, chromium-iron-zinc-spinelles, titanium-dioxides, copper-chromium-iron-spinelles, cobalt-alumina-spinelles and zirconium oxides.

10 Pastes especially suitable for the described usage have preferably the following viscous behaviour:

Viscosity test:

15 Equipment: Universal Dynamic Rheometer UDS 200 (dynamic viscosity. measuring device)  
Measuring apparatus:

Plate plate system; upper plate MP30, 25 mm diameter, 0°, sand blasted; lower plate sand blasted

20 Conditions: temperature when measuring was conducted: 23°C; gap width 0.5 mm; waiting time before measurement starts: 3 min.

Description: Verify that material is filled evenly in the gap and let the upper plate rotate to initiate measurement. Measure the average viscosity over 180 sec at a shear rate of  $10 \text{ sec}^{-1}$ . Reduce  
25 the shear rate to  $0.1 \text{ sec}^{-1}$ . Collect the recovery of the viscosity 40 sec after the reduction of the shear rate. Repeat measurements several times with freshly applied material.

The results are shown in Table 2.

Table 1

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Material	Value
Average viscosity at a shear rate of $10 \text{ sec}^{-1}$	$1.0 \times 10^4$ to $4 \times 10^4$ [mPas]
Average viscosity at $0.1 \text{ sec}^{-1}$	$10 \times 10^4$ to $160 \times 10^4$ [mPas]

measured 40 sec after shear rate reduction (viscosity recovery)	
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Pastes especially suitable for the described usage have the following abrasive behaviour:

Tooth brush wear and abrasion test. Comparison of physical properties with a conventional material

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Medium: Odolmed (tooth paste) : Water = 2 : 1      Cycles: 100, 000  
Load: 200 grams      Motion: Slow

10 Material in this test:

Bisphenol A diglycidyl acrylate 19 % by mass, urethane methacrylate 11% by mass, triethylene glycol dimethacrylate 22% by mass, silicon dioxide 23% by mass, silicon dioxide/polydodecanediol dimethacrylate 24,4 % by mass, and initiator 0.6% by mass.

15 Dentacolor Sirius (registered trademark); composition:

Matrix resin (urethane dimethacrylate, triethylene glycol dimethacrylate, dodecane diol methacrylate) 25.5% by mass; filler (silicon dioxide/polydodecanedioldimethacrylate, silicon dioxide) 74 % by mass; catalyst (camphorquinone) 0.5 % by mass; and trace quantity of pigment.

20 Comparison of physical properties data of preferred material and Dentacolor Sirius are shown in Table 2

Table 2:	Wear amount	Wear depth	Filling ration[%]	Surface roughness
Preferred material	0.1040 mm <sup>3</sup>	6.6 µm	47,4	0.41 µm
Dentacolor Sirius	0.1985 mm <sup>3</sup>	13.8 µm	78	0.85 µm